

Influence of microaliquation of liquid borosilicate sodium on stationary polarization of nickel

A I Mikhailov, A I Sotnikov, N D Vatolina, D A Nikitenko and A N Vatolin¹

Metallurgical Department, Ural State Technical University – USTU, Mira St.19,
Yekaterinburg, Russia

E-mail: anv@mtf.ustu.ru

Abstract. Influence of microaliquation of liquid borosilicate on stationary polarization of a nickel electrode is revealed. The equation describing the volt-ampere characteristics for a case of exponential dependence of component diffusion coefficients on its concentration in diffusion layer is proposed. Temperature and concentration dependences of the kinetic parameters which determine limiting diffusion currents of nickel ions in equimolar borosilicate melt are found.

1. Introduction

Ascertainment of linkage between structure of oxidic melts, their transport properties and the rate of electrochemical interaction with solid metals is one of the topical problems of physical chemistry. The important direction of explorations in frames of the specified problem is the experimental study of the influence of microaliquation of fluidic borosilicate and its anionic polymerisation on the form of stationary polarizing characteristics of metal electrodes and concentration dependence of limiting currents of cations diffusion.

It is known [1-4], that borate and borosilicate systems containing a small concentration of nickel oxide are inclined to the aliquation. The saturation concentration of NiO is insignificant and close to 3 mas %. At the attainment of this concentration nickel oxide precipitates out as a separate phase. The propensity of the systems to microaliquation should be discovered also at NiO concentration below the solubility limit. In a narrow concentration interval (0 - 3 mas %) the activity of a nickel oxide normalized on solid oxide grows from 0 up to sharply 1. That results in essential change of a melt structure and in difficult determination of concentration dependence of transport properties [2 - 4]. Therefore, borosilicate systems containing NiO are a convenient object to study the influence of microaliquation on a stationary over voltage of an electrode. From a practical point of view the exploration of similar systems can be interesting for development of new ecologically clean methods of nickel electrochemical extraction from oxidised ores.

2. Experimental

Cathodic polarization of a solid nickeliferous electrode in the melt of equimolar mixture of sodium, boron and silicon oxides with doping up to 3 mas % NiO was investigated using the potentiostatic method. In order to decrease the concentration of dissolved water the melt was degassed during two

¹ To whom any correspondence should be addressed.

hours at 1273 K to a residual pressure of the order of 10 Pa. The measurements were performed in the oxidizing air atmosphere in the temperature range of 1173 to 1323 K. The electrochemical cell consists of a corundum crucible filled in with an oxide melt and two electrodes, investigated and auxiliary, immersed into the melt. A polished butt-end of a nickel wire with a diameter of 4 mm and lateral surface protected by a corundum capillary was used as the investigated electrode. The auxiliary electrode was made of the same wire in a flat spiral form. The polarization of the auxiliary electrode was not taken into account because its surface contacting with the melt exceeded the working surface of the investigated electrode more than by two orders of magnitude. To achieve reproducibility of hydrodynamic conditions we used crucibles of identical size and electrodes with identical working surface. Changing the electrode potential from an equilibrium value with a step of 20 mV we measured a current through the cell. Electrical resistance of the electrolyte was determined by means of a microprocessor impedance analyzer working at a frequency of 15 kHz.

3. Results and discussion

Basing on the experimental dependences of current density on over voltage the concentration dependences of limiting diffusion currents were fitted (fig. 1). It can be seen that these currents values grow with an increase of nickel oxide concentration in the melt.

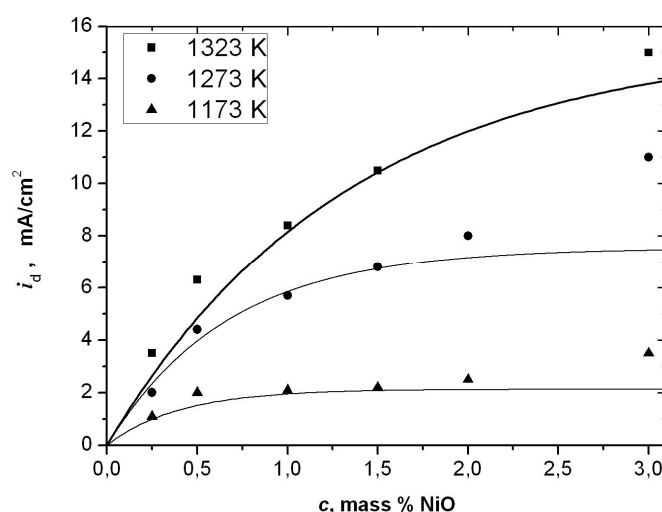


Figure 1. Concentration dependence of nickel ions limiting diffusion currents.

The non-linear concentration dependences of limiting currents testifies that the traditional concentration-polarization equation can not describe the volt-ampere characteristics satisfactory. Really, according to the equation the limiting current of diffusion (i_d) should be proportional to the volume concentration of nickel ions in the melt ($c_{Ni^{2+}}^V$):

$$i_d = zF \frac{D_{Ni^{2+}}}{\delta} c_{Ni^{2+}}^V, \quad (1)$$

to the contrary to our results.

Equation (1) was obtained basing on the assumption that the diffusion coefficient D is independent on concentration of a diffusing component in the diffused layer of the thickness δ . The revealed

discrepancy between the theoretical and experimental dependences allows conclusion that diffusion constants of nickel ion can change their values in the concentration range under study. Really, it was shown in [2 - 4], that the diffusion coefficient of nickel ions depends on NiO concentration in borosilicate melts and this dependence includes some extremums. According to [2-4] a small doping of NiO into the melt (up to 0.5 mas %) results in its depolymerisation and, accordingly, increase in diffusion coefficients of Ni^{2+} ions. At a further increase of NiO content up to 1.5 mas % atomic groups enriched with nickel oxide appear in the melt. The Ni^{2+} ions concentration outside the groups decreases, and the surrounding melt becomes more polymerized again. It results in significant (on 1 to 2 orders of magnitude) reduction of Ni^{2+} ions diffusion constants. At NiO concentrations of 1.5 to 3 mas % an increase of Ni^{2+} ionic mobility is observed, that, apparently, is connected with formation of contacts between the groups enriched with nickel oxide. When temperature raises the microaliquation effects become less pronounced, NiO solubility in the melt increases and extremums in the concentration dependence disappear.

The information on diffusion constants of nickel ions in the sodiumborosilicate melts [2, 3] was used for explanation of our results. At NiO concentration of 0.5 to 1.5 mas % the linear concentration dependence of the diffusion coefficient logarithm was revealed (fig.2).

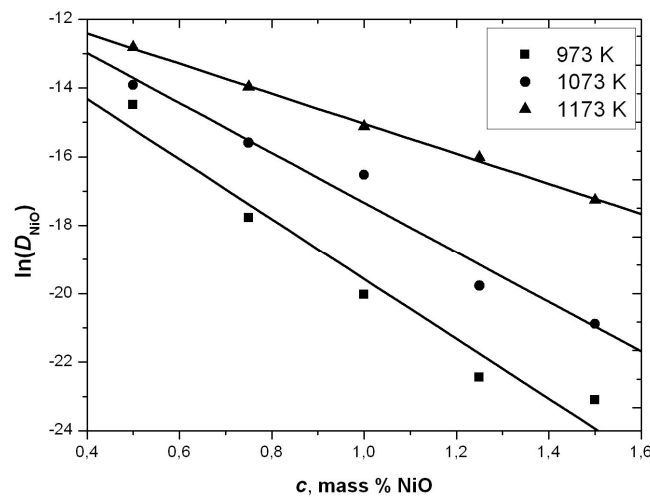


Figure 2. Concentration dependence of nickel ions diffusion coefficients in the $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ melt.

The experimental data are well approximated by the dependence:

$$D_{\text{Ni}^{2+}} = D_0 \exp(-kc_{\text{Ni}^{2+}}), \quad (2)$$

where D_0 and k are empirical constants. As at current densities close to limiting values of i_d the nickel ions concentration in a diffused layer δ varies from 0 up to $c_{\text{Ni}^{2+}}^V$, on can expect a significant change of the diffusion constants too. Let us set the derivation of the concentrating polarization kinetic equation for this case, using expression (2).

The linkage between current density and gradient of the nickel ions chemical potential can be presented as:

$$i = -\frac{zF}{RT} \left(D_{\text{Ni}^{2+}} c_{\text{Ni}^{2+}} \frac{d\mu_{\text{Ni}^{2+}}}{dx} \right)_{x=0} = -zF \left(\frac{dy}{dx} \right)_{x=0}, \quad (3)$$

where

$$dy = \frac{D_{\text{Ni}^{2+}}}{RT} c_{\text{Ni}^{2+}} d\mu_{\text{Ni}^{2+}}. \quad (4)$$

Supposing, similarly to Nernst model, that inside diffused layer δ the y value is proportional to coordinate, we receive:

$$i = zF \frac{y_s - y_V}{\delta}, \quad (5)$$

After finding the difference $y_s - y_V$, it is possible to get the final expression for the polarizing characteristic:

$$\frac{i}{i_d} + 1 = \frac{1 - \exp\left(-kc_{\text{Ni}^{2+}}^V \exp\left(\frac{zF\eta}{RT(1+p)}\right)\right)}{1 - \exp(-kc_{\text{Ni}^{2+}}^V)}, \quad (6)$$

in which the diffusion limiting current i_d depends on volume nickel ions concentration $c_{\text{Ni}^{2+}}^V$ nonlinearly:

$$i_d = \frac{zF}{\delta} (1+p) \frac{D_0}{k} \left(1 - e^{-kc_{\text{Ni}^{2+}}^V}\right). \quad (7)$$

The estimated limiting current values are compared with experimental ones in fig. 1. It is visible from the figure, that the calculation values coincide with experimental well at NiO concentrations of 0.5 to 1.5 mas %, i.e. in the interval where (2) is true. At a further increase of NiO content the concentration dependence of the diffusion constants changes, probably, because of formation of contacts between atomic groups enriched in nickel oxide and appropriate dimensional grid.

References

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